

APPENDIX A

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Advances in crosslinking technology

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Abstract: Different techniques used for crosslinking of polyolefins, focusing on cable and pipe production, are presented. Methods for measuring crosslinking and extrusion behaviour of crosslinkable polyethylene are discussed as well as additives for controlling the processing during extrusion. The development of new types of silane crosslinkable copolymers are presented in more detail.

Introduction

In the solid state polyethylene is a semicrystalline structure built up from crystalline regions, with amorphous parts in between. The amorphous regions are weak from a mechanical point of view, with few interlamellar links. When crosslinking polyethylene, chemical covalent bonds are formed which link the different regions together. A three-dimensional network is thus formed which drastically improves a large number of properties such as heat deformation, abrasion, viscous deformation, chemical, and stress cracking resistance. Impact and tensile strength are increased, shrinkage decreased and low temperature properties improved. Cross-linked products have shape memory which is used for production of heat shrinkable sleeves, tubes and films.

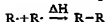
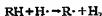
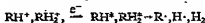
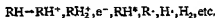
The improvement in high-temperature properties has been of big importance for the use of crosslinked polyethylene (XLPE) for power cable applications. By crosslinking low-density polyethylene (LDPE) which has a flexibility suitable for cable applications, but a rather low melting point (around 110°C), the maximum operating temperature is increased from 70 to 90°C and the short circuit rating from 130 to 250°C, resulting in saved costs and increased safety. Peroxide crosslinkable polyethylene has been used for about 20 years as power cable insulation. Due to its excellent dielectrical properties and the real life performance, as well as the ease of installation, it has replaced the old paper insulation in most parts of the world. Gradual utilisation of improved cable constructions, manufacturing processes and XLPE with improved homogeneity and cleanliness has resulted in production of up to 300 000 V cables today.

In hot-water pipe applications stiffer materials can be used and high-density polyethylene (HDPE), with its higher melting point, around 135°C, and better mechanical properties, is a natural choice. By crosslinking, the improvement in creep resistance results in pipes with longer life. The improvements in impact and chemical resistance are of importance for rotational moulded containers and pipes for transport of chemically aggressive media.

Today, three ways of crosslinking polyolefins are of commercial interest. The first commercial cross-linked products were produced by radiation in the mid 1950s.¹ Radiation crosslinking would probably be more widely used today if the peroxide crosslinking process had not been invented a few years later. The third technique silane crosslinking was introduced in the late 1960s with the development of the Sioplas technique.²

Radiation crosslinking

The different crosslinking techniques and processes used for polyethylene are summarised in Fig. 1. In both peroxide and radiation crosslinking the crosslinks are formed by combination of alkyl radicals. In radiation crosslinking these radicals are formed either by accelerated electrons (β^- -radiation) or by electro magnetic waves (γ -radiation). Its chemistry can be summarised as follows:^{3,4}



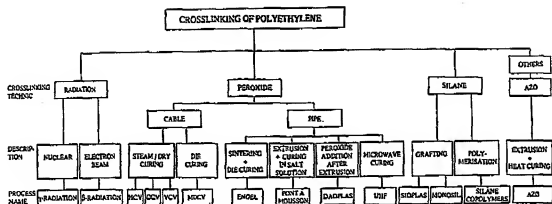


Fig. 1 Methods used for crosslinking of polyethylene.

γ -Radiation is a nuclear process and radiation from the ^{60}Co isotope is commonly used for laboratory experiments. The drawback with this source is that it cannot be "switched" off and its commercial use is mainly restricted to sterilisation of films and thin bodies.

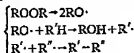
Electron beams (β -rays) produced in large accelerators are commercially used for crosslinking polyethylene. The energy required to penetrate 1 and 3 mm thick polyethylene is 0.55 and 1 mega-electronvolt (MeV), respectively.³

The main advantage with radiation crosslinking is that high output extrusion can be used as there is no risk of precurcuring. There are, however, several disadvantages in connection with this crosslinking operation. For example, high voltages are needed for crosslinking thick sections and circular objects have to be rotated, or several beams have to be used, in order to be evenly irradiated. The application of solid-state high-energy accelerators has reduced the price of high-energy accelerators,⁴ but investment costs are still considerable.

Peroxide crosslinking

General

As mentioned above the peroxide and radiation crosslinking are similar in that the crosslinks are carbon-carbon bonds formed by combination of alkyl radicals. Peroxides (ROOR) are compounds that form reactive radicals under the influence of heat. Ultra-high frequency (UHF) initiation has also been studied.^{2,5} Its commercial use is still very limited. The reaction scheme for peroxide crosslinking can be written simply as follows:



Peroxide crosslinkable polyethylene is mainly used for cable, pipe and rotational moulding applications. Peroxide-containing compounds have to be processed at low temperatures, where the decomposition of the peroxide is slow, in order to avoid precurcuring. This means that the risk of precurcuring is related to the melting point of the polymer. Today, major peroxide suppliers have a peroxide, 2,5-dimethyl-2,5-bis(*t*-butylperoxy)hexane-3 (DMTBH), available. This peroxide is claimed to give safe processing up to a temperature of 150°C ,^{6,10} compared with the most common peroxide for polyethylene, dicumylperoxide (DCP), which gives safe processing up to 120°C .

For vulcanisation, a heat treatment has to be applied on the extruded product. This is normally made on line directly after the extrusion step. The slow peroxide mentioned above (DMTBH) will need a residence time of 23 min at 180°C to reach 90% of its final cure level, compared with 7 min for DCP.⁹ As the crosslinking speed will have a big influence on the production speed the optimisation between safe processing and fast crosslinking is the key factor in this technology. These complex problems have led to the development of different crosslinking techniques for cable and pipe applications (see Fig. 1).

Peroxide crosslinking within the wire and cable area

For cable applications DCP, which is very suitable for LDPE, has been used for more than 20 years. Acceptable extrusion performance is achieved at a processing temperature between 125 and 140°C for the peroxide-containing compounds used. Streamlined flowpaths and use of conical screw tops are of importance to reduce the residence time. Screw cooling increases shear forces and residence time and should only be used when the compound is not properly mixed. With this level of care a production

period of about 1 week is commonly used before cleaning has to be done.¹¹

After the extrusion step, during which the polyethylene has been applied onto the conductor, the insulated conductor immediately enters the vulcanisation zone. During this step volatile by-products such as acetophenone, cumyl alcohol, methane, α -methylstyrene and water are formed.¹² In order to avoid formation of voids in the dielectric, the vulcanisation zone is pressurised in the range 12–20 bar. The vulcanisation tube is ended with a cooling section from which the cable core emerges into atmospheric pressure at a temperature of around 80°C. Steam at a temperature around 210°C was originally used for heating. It has the disadvantage, that it is diffusing into the insulation and condenses, leading to formation of about 10^5 – 10^6 microvoids per mm^3 .^{6,13} The water content in a steam-cured insulation is around 200 ppm close to the conductor, ~1000 ppm in the middle and 3000 ppm near the outside.¹³ The remaining water can negatively effect the long-time ageing performance of the cable as the risk of the electrical ageing phenomena, water treeing, will increase. The risk of water treeing can, however, today be considerably reduced by using water tree retardant XLPE.¹¹

These problems have led to the development of the dry-curing process where radiantly heated, circulated and pressurised nitrogen, or in some cases silicone oil or eutectic salts, are used as heat transfer media. This process does not add any other microvoids than the one generated by the decomposition of the peroxide, around $10^2/\text{mm}^3$.⁸ Dry curing has enhanced the electrical strength by 20%.⁶ One further advantage is that since the vulcanisation temperature is not related to pressure, as for steam curing, a higher temperature can be adopted leading to a faster crosslinking operation.

Three different types of vulcanisation lines are used for dry or steam curing, i.e. catenary (CCV), vertical (VCV) and horizontal continuous vulcanisation (HCV) lines. Horizontal lines can only be used for smaller diameter cables, CCV for medium and high voltage cables, while for the thickest insulations VCV lines have to be used. This is because the polymer melt is sensitive to the force of gravity during the vulcanisation step and a pear-shaped cable will otherwise be produced. The development of more viscous XLPE compounds and processes where the core can be twisted during vulcanisation has reduced this problem and cables with an insulation thickness close to 30 mm have successfully been produced in CCV lines.

Medium- and high-voltage cables normally consist of three peroxide crosslinkable layers applied in a triple extrusion process. A semiconductive layer consisting of a carbon black filled ethylene copolymer is extruded on the conductor, followed by

the much thicker insulation layer and the thin outer semiconductive layer. A typical CCV line for production of medium-voltage cable cores is shown in Fig. 2. A CCV line can be over 200 m long, while VCV lines are limited to about 80 m, because of the high cost associated with building a vertical structure.

Direct contact heating vulcanisation is another technique used for production of medium- and high-voltage cables, the so-called Mitsubishi-Dainichi continuous vulcanisation (MDCV) process. In an MDCV line a lubricated die around 25 m long is used for heating. The extruder is the driving part in this process, it is 'pushing' the insulated conductor through the die and in order to pressurise the vulcanisation step a brake is applied on the conductor.

Peroxide crosslinking within the pipe area

As mentioned above, stiffer material like HDPE has been of main interest for hot-water pipe applications. Higher melting point means that a much higher extrusion temperature has to be used than is the case for LDPE. This has complicated utilisation of peroxide crosslinking for this application and led to a development of different manufacturing processes (Fig. 1).

The *Engel process* was the first process developed for HDPE.^{14,15} In this process high-molecular-weight polyethylene with M_w around 500 000 is mixed together with peroxide and fed into a reciprocating plunger extruder. Under high pressure, i.e. about 2000–5000 bar, the granular polyethylene is sintered together. The product is then passed through a long heated die where the crosslinking takes place.

The *Pont d'Aousson process* is the one most similar to the techniques used in the cable field. HDPE with a lower molecular weight (M_w 200 000–500 000) is used¹⁶ and is mixed with peroxide and extruded into a pipe. The crosslinking is performed in a salt solution at temperatures above 200°C. The high extrusion temperature necessary for HDPE can, however, cause problems with surface finish.

In the *Daoplas technique* HDPE without peroxide is extruded into pipes or profiles. The peroxide is diffused into the extruded product by putting it into a surrounding media containing the peroxide. Peroxide decomposition takes place by heating above 160°C under pressure.

UHF crosslinking has been proposed for pipe applications.^{17,18} Peroxides used are sensitive to microwaves like 4-chloro-*tert*-butyl perbenzoate, di-*tert*-butylperoxyterephthalate, 3-*tert*-butyl peroxy-3(4-chlorophenyl) phthalide^{8,19} etc. The decomposition is accelerated by the internal heating of these

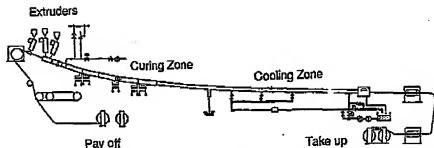


Fig. 2 A typical CCV line for production of triple extruded cables.

peroxides induced by increased dipole motions caused by the UHF electromagnetic field.

Besides peroxides, azo compounds are used for crosslinking of HDPE pipes.¹⁰ The technique has much in common with peroxide crosslinking. The azo compounds are decomposed under the influence of heat, forming nitrogen and radicals that abstract hydrogen from the polyethylene chain. The advantage for HDPE is that azo compounds are thermally more stable which simplifies the extrusion. The crosslinking is performed in a salt bath or in a vulcanisation tube at temperatures of about 240–270°C.

Peroxide crosslinking within the rotational moulding area

Peroxide crosslinkable compounds are used for rotational moulding as well. By optimisation of the flow and crosslinking properties of the compound, as well as the process parameters, the material is melted out whereupon crosslinking takes place in the same mould.

Extrusion and crosslinking performance

For measuring the crosslinking degree of XLPE three methods are mainly used: decaline extraction (ASTM D 2765), hot-set test (IEC 811) and rheometers.

The gel content measured by extraction for a fully cured XLPE compound lies around 80%. In the hot-set test, the heat elongation of dumb-bells is measured at a specific load and temperature, see Fig. 3. The heat elongation is about 80% for a fully cured peroxide crosslinked polyethylene. Silane crosslinked materials normally give lower values, a 70% gel content, and less than 50% heat elongation. For more detailed studies of the crosslinking performance of peroxide crosslinkable compounds rheometers have to be used.

Besides crosslinking speed and final cure level, the extrusion performance of peroxide-crosslinkable

HOT SET TEST

The heat deformation of cable insulation is measured at 200 °C with a load of 0.2 MPa (IEC 811)

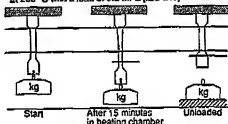


Fig. 3 Heat elongation measurement of crosslinked XLPE.

compounds have to be carefully controlled to reduce premature crosslinking. This can lead to formation of discoloured unmeltable particles, so-called scorch, that drastically reduce the breakdown and mechanical strength of the products.

To test the scorch sensitivity, several methods can be used. For example, long-time extrusion tests or measuring the increase in torque by the use of Brabender kneader or rheometers. So far, the authors have tested over 40 commercial and experimental cable compounds in the long-time extrusion test, where the XLPE is extruded at a temperature of 130°C for 72 h. A very low output is used in this test, 4 kg/h, which means that a screw speed close to 5 rpm is used. The test has been described in more detail elsewhere.¹¹ The residence time for three different screw speeds has been measured on this extruder by addition of one pellet of a titanium dioxide (TiO₂) masterbatch and measuring the amount of TiO₂ in the extrudate. As can be seen in Fig. 4, the residence time is close to 50 min at 5 rpm.

In the long time extrusion test the precuring properties of a compound are evaluated by collecting all scorch found in the extrudate. After the 72 h run the extruder is taken apart and all scorch deposits found are collected. Scorch deposits are always found at the screw top (no conical screw top is used), close to

TROESTER PE-SCREW 60 MM

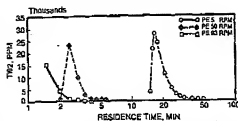


Fig. 4 Residence time distributions at different screw speeds (Tl_{02} content measured by X-ray fluorescence).



Fig. 5 Scorch deposits after long-time extrusion.

BRABENDER SCORCH TEST

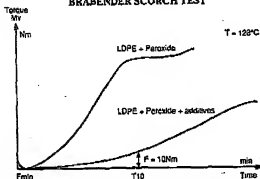


Fig. 6 Comparison of scorch performance measured with Brabender Kneader at 128°C.

the walls of the neck, the channel between neck and head and at the walls of the flow channels in the head. In Fig. 5, the scorch deposits of one of the best as well as the worst commercial cable compounds tested are shown. For the bad compound, scorch was also found in the extrudate.

As mentioned above, scorch resistance can also be measured in a Brabender kneader. In Fig. 6, torque curves of a base resin containing 2% dicumyl

peroxide and no further additives are compared with the 'good' compound discussed above. These two compounds have the same crosslinking performance, but the torque increase at a typical extrusion temperature, 128°C, is much slower. The additive in this compound is deactivating the radicals leading to molecular enlargement at the extrusion temperature level, but not at the higher crosslinking temperature level. The authors have found that the time it takes to increase the torque with 10 Nm from the minimum level (t_{10}) correlate with the amount of scorch found in the long-time extrusion test, and with the experience from the market. The additive-free sample gave a t_{10} value of 48 min while commercial compound needs more than twice as long, 101 min. The bad compound in Fig. 5, gave a t_{10} value of 60 min. Besides the additive package, the polymer structure and molecular weight distribution have to be optimised with respect to peroxide response, crosslinking and extrusion performance.

Silane crosslinking

The Sioplas process

In 1968 Midlands Silicones (Dow Corning) patented² the so-called Sioplas process. It is a two-step process not including the polymerisation step. By compounding, vinylsilane (normally vinyltrimethoxysilane) is grafted to polyethylene with peroxide as initiator. The most common peroxide used for grafting is 20 times smaller (~0.1%) than that used for peroxide crosslinking. The alkyl radicals formed by the peroxide will break the unsaturation in the silane and bind it to the polyethylene chain. A drop in melt flow rate is always observed during the grafting operation, due to the fact that the grafting reaction is a non-terminating reaction. Therefore, combination and other reactions will take place, before the radicals are inactivated. The grafting process is limiting the choice of antioxidants since many of them are effective radical scavengers and can inhibit the grafting reaction. Since aromatic amine stabilisers have a very low tendency to 'kill' radicals, many of the Sioplas compounds have a yellow colour due to these. The grafting step is schematically explained in Fig. 7. After the grafting step Sioplas compounds are pelletised and stored.

In the second step of the Sioplas process normally 5% of a catalyst masterbatch is dry-blended with the grafted compound and the final product extruded. Crosslinking takes place before the production line in a water bath or in a sauna at elevated temperatures, 60–90°C. The active catalyst is usually an organo-tin derivative like dibutyltin dilaurate. During the influence of the catalyst, water is reacting with the methoxy groups forming silanol groups, which

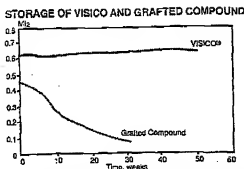


Fig. 10 Storage stability test by measuring melt flow rate as a function of storage time.

Table 1. Design stresses at 40 and 60°C

Temperature (°C)	Design stress (MPa)
40	32
60	25

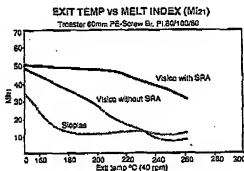


Fig. 11 Processability test of silane crosslinkable compounds; 5% catalyst masterbatch added.

In order to increase the processing window of these copolymers to a similar level of that of thermoplastic compounds, intensive work to develop a scorch-retardant additive (SRA), an additive that stops molecular enlargement reactions during extrusion, has been performed. This work was implemented 3 years ago and has resulted in big improvements in processability and gives a compound which is not sensitive to high temperatures, Fig. 11. SRA also makes the polymer more insensitive for residence time, a property which is of major importance during tool changes and interruptions on the production line, when the screw speed is reduced to a minimum. As seen in Fig. 4, the screw speed has a great influence on the residence time. At 93, 50 and 5 rpm, a detectable amount of TiO_2 is

found after 4, 6 and 50 min, respectively. A residence time of 50 min is a rather tough condition for a crosslinkable compound and without any SRA the surface finish quickly deteriorates, and very often it is impossible to get rid of formed gels without taking the extruder apart and cleaning it. In one of the tests for evaluating silane crosslinkable compounds, a thin tape is produced, at a temperature of 210°C, 30 rpm, for 0.5 h, whereupon the extruder is stopped for 20 min. Without SRA there are a large number of lumps in the extrudate when starting up and these cannot be removed without taking the extruder apart and cleaning it. With SRA-containing compounds excellent surface finish is obtained 2 min after restarting the extruder. The formation of die drool, which is a problem for silane crosslinkable polyethylene, is also significantly reduced by the compatible and non-volatile SRA.

The reason for the effectiveness of the SRA is that it reacts with water faster than the polymer itself during extrusion conditions. Will it then effect the crosslinking speed, another very important property? The crosslinking speed of Visico, with and without SRA, is compared by crosslinking 2 mm thick tapes in water at 60 and 90°C, for 1, 4, 8 and 20 h (Fig. 12). At 90°C no significant difference can be seen. At 60°C, there is a clear difference at the shortest crosslinking time, 1 h. No gel at all is observed for the SRA-containing compound while 30% is achieved without. At the longer crosslinking times the same gel contents are obtained. The same behaviour would probably have been seen at 90°C, if gel at shorter crosslinking times had been measured. The SRA also stops the crosslinking reactions at the lower crosslinking temperatures, but when it is consumed the crosslinking reaction goes faster than without the additive. The net effect is that the time to reach over 50% gel content is the same as without the SRA. In practice, the observed difference is of minor importance as a crosslinking level over 50% has to be reached for all applications.

Applications. The main applications for Visico are as insulation for low-voltage and signal cables, where it has been used for 7 years in commercial production on both PVC and polyethylene extruders. Visico is also working on normal polyethylene pipe extruders as well as the longer Monosil lines, where the line speed can be increased 30% compared to the normal Monosil materials.

A pressure test curve showing the circumferential stress in the pipe wall, i.e. the hoop stress as a function of failure time (T_f), can be described, according to Iwanson and Eriksson,²³ in three stages, I-III (Fig. 13). Failures at stage I are caused by ductile creep, stage II failures have slow stress cracking as the predominant failure mechanism and stage III is

caused by chemical degradation of the polymer. When properly crosslinked XLPE pipes, do not show any stage II on the pressure test curve, only stage I and stage III failures occur.²³

In order to establish a design basis for pipes made out of Visico, stage I pressure testing, according to ISO 1167 with water as the inside and outside media, has been made at 40 and 60°C. Extruded pipes (32 × 3 mm) were crosslinked in a water bath at 90°C for 16 h before testing. The gel content was 73% as measured by dioxane extraction. The pipes were produced with a diameter draw down of 35% and 18% on the pipe wall. It is important to adjust the draw downs carefully as high draw downs, over 50%, have shown a negative effect on the pressure

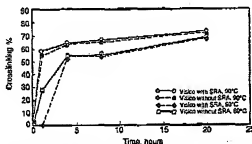


Fig. 12 The effect of scorch-retardant additive on the cross-linking speed: 1.8 mm thick tape crosslinked in waterbath at 60 and 90°C, respectively.

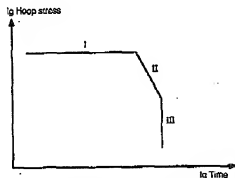


Fig. 13 Creep rupture curve, polyethylene.

Table 2. Pressure testing of Visico, water/air

Test temperature (°C)	Failure time stage III (h)	Calculated lifetime at 60°C (h)
100	20 000	985 000 (112 years)
95	> 25 000	> 758 000 (> 86 years)
80	> 25 000	> 176 000 (> 20 years)

test performance. The pressure test curves for these pipes are presented in Fig. 14.

Linear regression and an applied safety factor, f_s , larger than 1.3 gives the design stresses at 40 and 60°C for 50 years lifetime as shown in Table 1.

The design stresses obtained are the same as the ones for LDPE 3-2 and 2-5 MPa for 20°C and 50 years. The same pipe dimensions and couplings can be used for Visico at 40 and 60°C, 50 years, respectively. Further tests on the chemical degradation behaviour are, however, needed to confirm this.

The chemical lifetime of Visico has been tested according to ISO 1167 at 100, 95°C and 80°C with inside media water, and outside media air. Table 2 shows the results obtained so far. At 100°C, stage III occurred at a little over 20 000 h. At the lower testing temperatures, no breaks have yet occurred after nearly 3 years testing. To calculate corresponding lifetime at 60°C an Arrhenius calculation with an acceleration factor of 2.65/10 K has been used in accordance with the proposal in ISO/TC 138/WG 5. As can be seen in Table 2 the results indicate a lifetime much above 50 years at 60°C.

The results clearly show that Visico can easily be extruded into crosslinkable pipes or profiles and that it has excellent long time properties. It is an interesting product for such applications as

- flexible hot-water pipes for ground heating such as melt away pipes, low-temperature district heating, under-floor heating and central heating;
- flexible pipes for transport of aggressive media at elevated temperatures;
- shrink sleeves for cable and pipe connections; and
- foamed crosslinked profiles.

One disadvantage with Visico in the pipe field is of course that it does not fulfil some existing standards for hot-water XLPE pipes such as DIN 16892 which prescribes HDPE. Another fact is that we are talking

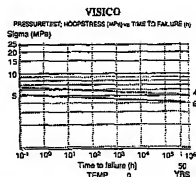


Fig. 14 Pressure test water/water at 40 and 60°C.

about an LDPE product and therefore, it cannot be used for higher pressure applications. However, the excellent properties of the Visico product should enable it to be a complement to conventional HDPE XLPE materials and Sioplas LD-materials which are used in applications where the above-mentioned standards are of no importance and where relatively moderate pressures are used.

Interesting results have also been obtained from other application areas. Visico gives an increase in dart drop of three to five times and an increased shrink for cold stretch films. For shrink sleeve applications the soft terpolymer is of particular interest. Best results are achieved when it is mixed with thermoplastic polymers in order to decrease the final gel content from around 75% to 60–50%. Visico works well in injection- and blow-moulding machines. In addition, it is an interesting product for coating applications as it gives a very high adhesion to different substrates, for example, aluminium, steel and glass.^{24,25}

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